

H-COAL SLURRY OIL COMPOSITION AND PROCESS PERFORMANCE

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INTRODUCTION

The H-Coal process, developed by Hydrocarbon Research, Inc., is a catalytic coal hydrogenation in which the coal is contacted with, usually, an alumina supported Co/Mo, or similar catalyst in an upflowing fluidized bed. The distinguishing features of the process are the reactor internals, which allow for fluidization of the catalyst bed, and catalyst addition and withdrawal systems to allow maintenance of the catalyst activity. The 3 TPD process development unit (PDU), operated by HRI at Trenton, NJ, has been used to study feed coal and space velocity effects, and to provide design data for scale-up of the process. A schematic of the unit (Figure 1) shows that the coal is fed to the reactor as a slurry with two recycle components. The hydroclone overflow (HO) contains distillate, non-distillate oils (resid), and solids. The clean oil tank (COT) is a surge vessel containing atmospheric still bottoms and vacuum still overhead. The amounts of these distillates in the clean oil tank can be independently varied.

An interest in the composition of these recycle oils, and how their composition is related to process performance, was the motivation for a recently completed program to analyze daily samples of recycle slurry oils from H-Coal PDU Runs 5, 8 and 9 by a variety of analytical techniques, and to relate the composition data to process performance in those PDU runs. PDU Runs 5 and 8 were made with Illinois 6 coal while PDU 9 used Kentucky 11 coal^(1,2,3). PDU Runs 5 and 9 were made in the Syncrude mode (space velocity = 31) while PDU Run 8 consisted of operations in both the Fuel Oil and Intermediate modes (Table 1). Daily samples of the clean oil tank and the hydroclone overflow were taken by HRI and shipped to CCDC for analysis. The analytical techniques used and the information desired from each are given in Table 2. The object of the study was to determine the relationship between slurry oil composition and process performance in eight specific areas:

1. Changes in the slurry recycle stream composition during startup.
2. The manner in which the process reaches steady state operation during startup.
3. The composition of the recycle stream during stable operation.
4. The changes in recycle composition in response to planned variations in process variables.
5. Changes in the recycle composition which cause or result from unplanned upsets in the process operation.
6. Changes in the recycle composition as evidence of changes in catalyst activity.
7. Differences in recycle composition as a function of space velocity (mode).
8. Differences in recycle composition as a function of feed coal (same space velocity).

In making interpretations of these data it is important to recognize that there are two ways in which the data can be expressed. The recycle slurry oil characterizations can be given as compositions, or intensive variables. For example, the weight percent

of benzene solubles in the recycle resid represents the nature of the material that is being recycled, without reference to the amount. Alternatively, the data can be expressed on a recycle rate, or extensive variable basis. Thus, the pounds of benzene insolubles recycled per pound of coal fed reflects both the composition of the recycle resid, and the total recycle rate of that resid. Both the composition and recycle rate data can be used to draw conclusions regarding steady state performance. In the work described here, all conclusions concerning steady state performance are based on a statistical treatment of the data which compares variations in the data with the experimental uncertainty of the measured variables. The mathematical basis of this treatment is described in the first topical report prepared under this contract⁽⁴⁾. The results presented below are abstracted from the much more extensive body of data included in the two topical reports and final report prepared under this contract^(4,5,6).

The purpose of this paper is to illustrate the major conclusions reached in this study. Therefore, confirming results of other analyses are not generally presented.

COMPARISONS OF RECYCLE COMPOSITIONS

Because H-Coal is a hydrogenation process, ¹H-NMR was expected to provide a useful measure of recycle oil composition. Table 3 presents average ¹H-NMR distributions for PDU Runs 5 and 9 and for the two space velocity periods of PDU Run 8. The periods of Runs 5 and 9 used for averaging were chosen to represent the best approach to steady state in those runs. Because of a number of upsets over the first 16 days, we could not identify steady state periods for PDU Run 8, and all the data were used to calculate averages. Comparing first the results from Runs 5 and 8 (both Illinois 6 coal) we see that the higher space velocities produce a less aromatic recycle distillate. Since hydrogenation severity decreases with space velocity this was unexpected. The gain in aliphatics between the Syncrude, Fuel Oil and Intermediate space velocities is seen in the alkyl alpha and gamma protons, which measure long chain aliphatics, such as paraffins. These differences in distillate composition may reflect the fact that lower distillate yields at the higher space velocity mean that the recycle distillate will see more passes through the unit. Of course, the operability difficulties encountered in PDU Run 8, and the intentionally divided nature of that run, make firm conclusions unlikely.

PDU Run 9 (Kentucky 11 coal, Syncrude mode) gives a less aromatic recycle distillate than PDU Run 5 (Illinois 6 coal, Syncrude mode), though the difference is not as great as between PDU Run 5 and the Intermediate mode of PDU Run 8. Apparently, space velocity has more effect on recycle distillate composition than feed coal.

Selected samples of the recycle distillates from the three runs were used to extract Indiana V coal in a microautoclave at two standard conditions. The results (Table 4) show that all of the recycle distillates are good liquefaction solvents. The conversions to THF solubles are generally in the 70-80% range, and these results are indicative of good liquefaction solvents⁽⁷⁾. Differences which occur in a given run, and among the different runs, indicate that recycle distillates produced in the Syncrude mode are better liquefaction solvents than those from either the Intermediate or Fuel Oil modes. In PDU Run 5 there was a general tendency toward improved solvent quality as the run progressed. In PDU Run 9 the trend is reversed, although the conversions obtained with the PDU Run 9 distillates are equivalent to or better than those from PDU Run 5. For PDU Run 8 the two days shown compare conversions for distillates produced in the Fuel Oil mode with distillates produced in the Intermediate mode operation. The distillates from the Intermediate mode are consistently poorer, and in some cases by a large margin, than those from the Fuel Oil mode. This is consistent with data shown in Table 3 giving the average NMR distributions of these distillates, which show a surprisingly high concentration of alkyl beta and gamma protons for distillates produced at the Intermediate space velocity.

While the recycle distillates were qualitatively similar, the recycle resids (975°F⁺, THF soluble) showed a much greater variation in composition, primarily as a function of

space velocity. Table 5 shows that the recycle resid from PDU Runs 5 and 9 (Syncrude) averaged around 49% oils (hexane solubles). The recycle resid in PDU Run 9 had a somewhat higher preasphaltene and lower asphaltene content than the recycle resid from PDU Run 5. However, the recycle resid in PDU Run 8 showed much lower oils content and much higher preasphaltenes content than for either of the Syncrude runs. This lower quality recycle resid in PDU Run 8 may have been related to (either as cause or effect) the operability problems which occurred in that run.

APPROACH TO STEADY STATE RECYCLE COMPOSITION

The data from PDU Runs 5 and 9 allow us to draw several conclusions concerning the approach to a steady state recycle slurry oil during those two runs. Because of the fragmented nature of PDU Run 8 we are not able to draw any conclusions concerning steady state operation from the data for that run. The majority of the data from PDU Runs 5 and 9 indicates that the recycle resid composition, but not the recycle rate, reached steady state between days 10 and 15. The recycle resid composition in PDU Run 5 does show some variation after day 20 of that run, when the hydrogen partial pressure was increased from an average of 1600 psig for the first 20 days of the run to an average of 1860 psig during the last 10 days. However, this appears to be an adjustment to a new equilibrium composition as opposed to a long term variation in the recycle resid composition. The plot of the ratio of benzene solubles to insolubles in the THF soluble recycle resid during PDU Runs 5, 8 and 9 (Figure 2) demonstrates this conclusion.

In contrast to the behavior of the recycle resid composition, the recycle rate of the resid did not reach steady state in PDU Run 9. This is illustrated in Figure 3, which shows the recycle rates of oils, asphaltenes and preasphaltenes on a lb/lb coal fed basis. Because the composition of the recycle resid reached steady state by about day 12, the plots are nearly parallel after that point. However, all three show steady increases throughout the 30-day run. A more rigorous treatment of the data⁽⁶⁾ shows that the preasphaltene recycle rate reached an apparent steady state by about day 25. These results are important since a steadily increasing resid recycle rate tends to reduce the apparent resid yield from the unit. Therefore, the recycle composition can have a direct and immediate impact on the perceived unit performance.

Two measures of the recycle distillate composition, the ratio of aromatic to aliphatic protons, and the concentration of phenolic-OH in the clean oil tank, are shown in Figures 4 and 5, respectively. These data demonstrate that the recycle distillate composition did not reach steady state in PDU Run 9. The data on samples from PDU Run 5 indicate a steady state recycle distillate composition sometime near the midpoint of that run. However, the data from PDU Runs 5 and 9 are very similar up to about day 20 of those runs, and the behavior of the samples from PDU Run 5 after day 20 may have been influenced by increased hydrogen partial pressure, as discussed above. Note that an increase in hydrogen partial pressure would tend to decrease both the aromatic-to-aliphatic ratio and the concentration of phenolic-OH. This could compensate for declining catalyst activity at the end of PDU Run 5.

These data and others concerning the approach of the recycle resid and distillate compositions to steady state indicate that the rate of catalyst deactivation for the larger resid molecules is more rapid than the rate of catalyst deactivation for the smaller distillate molecules. In other words the catalyst has reached a steady state with respect to conversion of the resid to distillate range material by day 10-15 of both PDU Runs 5 and 9. However, the catalyst activity with respect to hydrogenation of the distillate is still declining at the end of the 30 day run.

CONCLUSIONS

The major conclusions drawn from this work are:

- Startup solvent is rapidly replaced in PDU operation. Any aromatic startup solvent of the appropriate boiling range should suffice if it is physically compatible.

- Aromaticity of recycle oil increases during run with declining catalyst activity. Distillate aromaticity reached steady state in PDU 5 but not in PDU 9, perhaps because of increased P_{H_2} after day 20 of PDU 5. Same is true for hydroxyl contents of recycle distillates.
- Composition of recycle resid reached steady state in PDU Runs 5 and 9, by about day 12, but changed in Run 5 coincident with increased P_{H_2} .
- Recycle rate of resid did not reach steady state in PDU 9, although composition did. Situation in PDU 5 was complicated by increased P_{H_2} .
- Recycle resid in PDU 8 was much higher in preasphaltenes than PDU 5 or 9, probably related to operability problems.
- Recycle distillates were qualitatively similar regardless of mode or coal. All are good liquefaction media.
- PDU 5 and 9 data indicate a fast catalyst deactivation for resid hydrogenation (10-15 days) and a slower catalyst deactivation for distillate hydrogenation (> 30 days).
- Kentucky 9 and Illinois 6 coals give similar slurry recycle oils at the Syncrude mode. Differences among Fuel Oil, Intermediate and Syncrude space velocities, with same coal, are greater.

This work was supported by U.S. DOE Contract DE-AC05-79ET14503.

REFERENCES

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Table 1
H-Coal PDU Runs Studied

<u>PDU Run</u>	<u>Coal</u>	<u>Space Velocity (lb/hr-ft³) Mode</u>	<u>Operations Note</u>
5	Illinois 6	31 (Syncrude)	Increased P _{H₂} after day 20.
8	Illinois 6	78 (Fuel Oil) 50-65 (Intermediate)	Operating problems caused by plugging.
9	Kentucky 11	31 (Syncrude)	Uneventful.

Table 2
Analytical Techniques

- ¹H-NMR (COT, HO Distillate, HO Resid)
 - Hydrogen Distributions
 - Donatable Hydrogen
- LIQUID CHROMATOGRAPHY (HO Resid)
 - Solvent Fractionation (Oils, Asphaltenes, Preasphaltenes)
 - Chemical Functionalities
 - Molecular Size Distribution
- GC/MS AND REVERSE PHASE LIQUID CHROMATOGRAPHY (COT and HO Distillates)
 - Detailed Compositional Analysis
 - Characteristic Parameters
- ¹⁹F-DERIVATIZATION AND ¹⁹F-NMR
 - Hydroxyl (OH) Content
- MICROAUTOCLAVE
 - Empirical Measure of Solvent Quality

Table 3
Average ¹H-NMR Distributions
of Hydroclone Overflow Distillates

<u>PDU Run</u>	<u>Period</u>	<u>Mode</u>	<u>Average ¹H-NMR Distributions, Hydroclone Overflow Distillates</u>						
			<u>Cond. Ar</u>	<u>Uncond. Ar</u>	<u>Cyclic α</u>	<u>Alkyl α</u>	<u>Cyclic β</u>	<u>Alkyl β</u>	<u>γ</u>
5	12-30	Syncrude	26.7	11.1	17.3	12.2	11.9	13.5	7.3
8	3-15	Fuel Oil	26.6	9.2	17.5	11.9	12.2	15.3	7.3
8	17-21	Intermediate	21.6	8.6	16.5	11.8	12.5	19.4	9.5
9	10-26	Syncrude	22.4	9.7	17.5	12.2	13.6	16.2	8.4

Table 4

Microautoclave Extractions of Indiana V Coal With H-Coal
Recycle Distillates - Conversion to THF Solubles, Wt % MAF Coal

PDU RUN	5		8			9	
Sample	HO	COT	HO	COT		HO	COT
	Day		Day			Day	
EQ Conditions	3	80.6 69.8	--	-- --		3	85.7 81.0
	12	79.6 76.5	13	73.8 72.3		19	79.9 76.8
	25	77.9 77.3	20	72.9 62.3		26	77.6 75.9
	Avg	79.4 74.5		73.4 67.3			81.1 77.9
KIN Conditions	3	76.3 74.8	--	-- --		2	78.2 75.3
	12	80.8 74.3	13	82.7 73.6		19	78.7 72.7
	25	83.3 75.0	20	70.4 68.9		26	79.8 73.9
	Avg	80.1 74.7		75.6 71.2			78.9 74.0

EQ - 750°F, 30 min, 2/1 solvent/coal
KIN - 750°F, 10 min, 8/1 solvent/coal

Table 5

Solubility Fractionation of Hydroclone Overflow THF Soluble Resids

PDU Run	Period	Mode	Average, wt % THF Soluble Resid		
			Oils	Asphaltenes	Preasphaltenes
5	12-30	Syncrude	49.0	32.9	18.1
8	11-15	Fuel Oil	28.4	32.8	38.8
8	17-23	Intermediate	33.7	33.6	32.7
9	10-30	Syncrude	48.5	27.4	24.1

Figure 1
H-Coal Process Simplified Flow Diagram

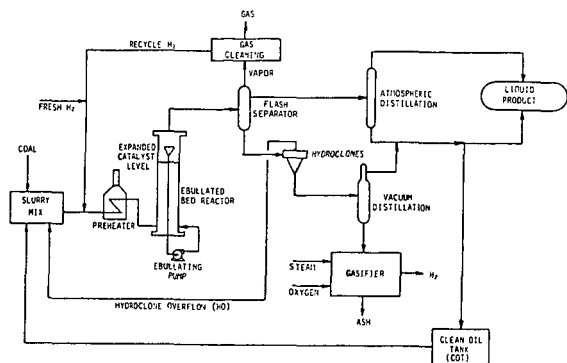


Figure 2
Comparison of Benzene Soluble/Insoluble Ratios
Recycle Resids - PDU Runs 5, 8 and 9

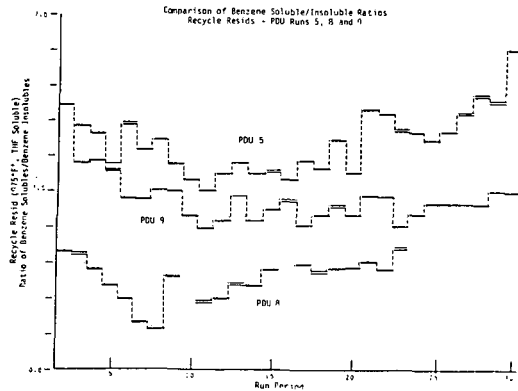


Figure 3
LCF Separation of HO THF Soluble Resid
H-Coal PDU Run 9

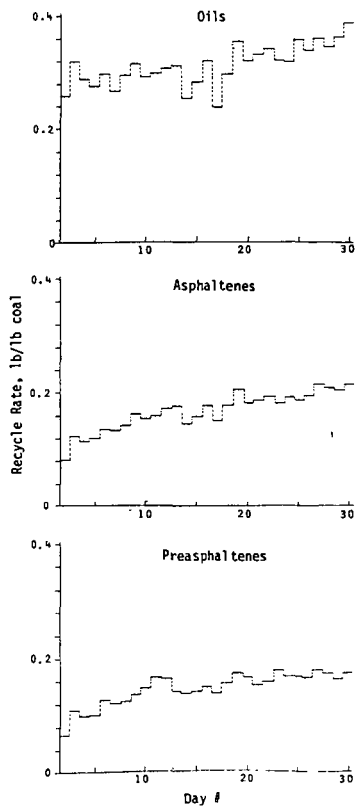


Figure 4

Ratio of Aromatic/Aliphatic Protons,
Total Recycle Distillate
H-Coal PDU Run 5 and 9

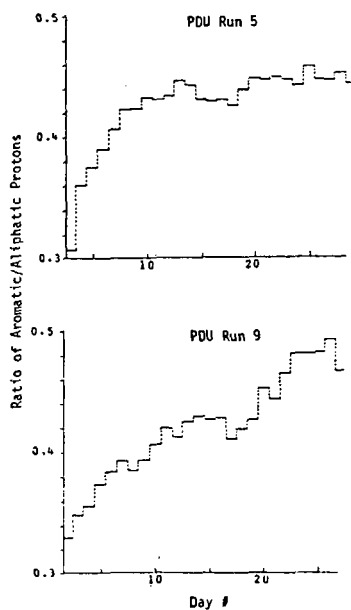


Figure 5

Concentration of Phenolic -OH by ^1H -NMR
COT Samples
H-Coal PDU Runs 5, 8 and 9

